

THE BEHAVIOUR OF ORGANIC SOLIDS ON THE SURFACE OF WATER

BY G. V. L. NARASIMHA MURTI AND T. R. SESHADRI
(From the Department of Chemistry, Andhra University, Waltair)

Received October 24, 1938

THE peculiar behaviour of camphor on the surface of water is a classical example of a general phenomenon characteristic of many solid organic compounds. A number of other substances have been more recently found to exhibit a similar behaviour (*vide* Geppert¹, Edwards² and Ramdas³). The factors determining these movements on the surface of water seem to be rather complex. Undoubtedly the non-uniform lowering of the surface tension is the major factor. For the vigour and persistence of the movements the substance which spreads as a film must be capable of subsequent diffusion inside the bulk of the liquid by solution or of leaving the surface by vaporisation. Since the lowering of the surface tension and the solubility of a substance with reference to a particular solvent are dependent largely upon its chemical nature, a large number of chemical compounds belonging to different groups have now been examined with respect to their behaviour on the surface of water.

In order that the observations may be correct it is very necessary that the utmost cleanliness be observed. The vessels used, cylindrical glass troughs 6" in diameter, were submitted to treatment with hot chromic acid followed by thorough washing with running tap-water. Wherever the purity of the samples was doubted they were recrystallized from suitable solvents, dried and the pure dry samples employed for the investigation. Touch of the fingers was scrupulously avoided as it was usually sufficient to impair, if not arrest, the movements in many cases by communicating a film of grease to the water surface. The substance was generally added with a spatula (freed from grease) from the least possible distance so as to minimise any mechanical disturbances and the water surface was as far as possible protected from air draughts. From the results of observation substances have been classified into three groups: A, B and C. Those that show vigorous movements are placed under A, those that show slow movements under B and the indifferent ones under C.

A	B	C
ACIDS		
1 Acetyl-salicylic 2 <i>o</i> -Amino benzoic 3 α -Amino butyric 4 Amygdalic 5 Benzoic 6 Cinnamic 7 Citraconic 8 Glutaric 9 Maleic 10 Malic 11 Malonic 12 Mesaconic 13 β -Naphthalenesulphonic 14 <i>o</i> -Nitrobenzoic 15 Phenyl acetic 16 Phthalic 17 Salicylic 18 Succinic	1 <i>m</i> -Amino benzoic 2 Diphenic 3 Fumaric 4 Hippuric 5 Proto-catechenic	1 <i>p</i> -Amino benzoic 2 Gallic 3 Naphthionic 4 Palmitic 5 Stearic 6 Sulphanilic
ANHYDRIDES		
1 Succinic 2 Phthalic	nil	nil
CARBONYL COMPOUNDS		
1 Antipyrin 2 Benzophenone 3 Camphor 4 Coumarin 4 Dimethyl- γ -pyrone 6 Menthone 7 <i>o</i> -Nitrobenzaldehyde 8 Quinone 9 Vanillin	nil	1 Anthraquinone 2 Michler's ketone 3 <i>p</i> -Nitrobenzaldehyde

A	B	C
AMIDES AND AMINO COMPOUNDS		
1 Acetamide	1 Benzanilide	1 6-Aminocoumarin
2 <i>o</i> -Acetotoluide	2 Diphenylamine	2 Benzidine
3 Benzamide	3 <i>p</i> -Phenylenediamine	3 Carbazole
4 Benzenesulphonamide	4 Phthalimide	4 Diphenylurea
5 Chloracetamide	5 <i>m</i> -Nitraniline	5 Hydrazobenzene
6 α -Naphthylamine		6 Malonamide
7 <i>o</i> -Nitroaniline		7 β -Naphthylamine
8 <i>m</i> -Phenylenediamine		8 <i>p</i> -Nitroaniline
9 <i>o</i> -Phenylenediamine		9 Oxamide
10 Phenylsemicarbazide		10 Oxanilide
11 Propionamide		11 Succinamide
12 Salicylamide		
HYDROXY COMPOUNDS		
1 Borneol	1 7-Hydroxy-4-methyl coumarin	1 Nitroso- β -naphthol
2 Hydroquinone		2 Phenolphthalein
3 α -Naphthol		3 Quercetin
4 β -Naphthol		4 Tetrahydroxy-anthraquinone
5 <i>m</i> -Nitrophenol		
6 <i>o</i> -Nitrophenol		
7 <i>p</i> Nitrophenol		
8 Pyrocatechol		
9 Quinhydrone		
10 Resorcinol		
ESTERS		
1 Glyceryltribenzoate	1 Phenyl benzoate	1 4-Methyl-umbeliferone acetate
	2 Phenyl salicylate	2 Acetyl-quercetin

A	B	C
HYDRO-CARBONS		
Nil	Nil	1 Acenaphthene 2 Anthracene 3 Diphenyl 4 Naphthalene 5 Phenanthrene 6 Triphenyl-methane
MISCELLANEOUS		
1 <i>p</i> -Nitroanisole 2 <i>p</i> -Nitro-toluene 3 Brucine	Nil	1 Azo-benzene 2 <i>m</i> -Dinitrobenzene 3 Dinitronaphthalenes (1 : 5 and 1 : 8) 4 <i>p</i> -Dibromobenzene 5 Hexachlorobenzene 6 α -Nitronaphthalene 7 Congo red.

The above list is neither complete nor comprehensive and various factors have limited the availability of suitable compounds. It is not possible therefore to venture any generalisation. But certain outstanding features may be noticed. There are certainly wide variations in the behaviour of substances. The hydrocarbons as a rule do not exhibit any movement. This seems to agree with the observations of Ramdas regarding the behaviour of liquid hydrocarbons. The introduction of a nitro group seems to have a varying influence. Nitrotoluene exhibits vigorous movement whereas *m*-dinitrobenzene, α -nitronaphthalene and dinitro-naphthalenes show no movement. Halogen substitution does not favour movement as can be seen from the behaviour of *p*-dibromobenzene and hexachlorobenzene.

The carboxylic acids and anhydrides in general exhibit vigorous movements. In regard to these the following points are noteworthy. Maleic acid comes under A and its isomer fumaric acid belongs to B. *o*-Amino-benzoic acid (A) differs from its isomerides *m*-amino-benzoic acid (B) and *p*-amino-benzoic acid (C). Only a few of the acids come under C. The presence of palmitic and stearic acids in this group may be easily understood

because they saturate the surface immediately. Obviously the influence of the COOH-groups, which in general favours rapid movement, can be completely controlled by other factors. As a rule carbonyl compounds come under A, none under B and a few under C. So the carbonyl group may be considered as one favouring quick movement. The amides and amino-compounds are represented in all the three categories. It is to be noted that here also the position of the groups affects considerably the behaviour of the substances. As examples the isomeric nitroanilines, naphthylamines and phenylenediamines may be mentioned. The simpler hydroxy compounds belonging to the group of phenols exhibit good movement whereas those having larger sizes and complex structures have very little movement. Esters in general do not exhibit vigorous movements. The introduction of an aliphatic residue favours the movements as in the case of glyceryltribenzoate.

Name of the substance	Percent lowering of surface tension	Classification of the movement
1 Phenylacetic acid ..	32.46	A
2 Camphor ..	25.85	A
3 Dimethyl- γ -pyrone ..	21.23	A
4 Maleic acid ..	12.22	A
5 Benzoic acid ..	11.60	A
6 Coumarin ..	8.01	A
7 Succinic acid ..	7.94	A
8 Phthalic acid ..	4.72	A
9 <i>p</i> -Nitrotoluene ..	4.60	A
10 <i>o</i> -Nitrophenol ..	3.30	A
11 Phthalimide ..	2.40	B
12 Fumaric acid ..	1.30	B
13 Diphenylamine ..	0.92	B
14 Anthracene ..	< 0.3	C
15 Diphenyl ..	< 0.3	C
16 Hydrazobenzene ..	do.	C
17 Naphthalene ..	do.	C
18 Sulphanilic acid ..	do.	C

With a view to get an idea as to the relative extent of lowering of the surface tension of water produced by substances which exhibit the movements and also to correlate the behaviour of the substances with their effect on the surface tension we determined the surface tension of the solutions of a few typical compounds. In each case excess of the substance was shaken with water for fifteen minutes and the surface tension of the filtered solution determined by the capillary rise method at 27° C. The results of our findings are given in the above table.

The movements exhibited by phenyl-acetic acid are the most spectacular of all. They are by far more vigorous than those of camphor or *p*-toluidine or any other vigorously moving substance. Its position in the table above is quite consistent with its remarkably vigorous movements. Hydrocarbons and other inert substances belonging to the class C have very negligible effect on the surface tension of water, the percentage differences being within the limits of experimental error. Substances which lower the surface tension by 3 or 4 per cent. are capable of exhibiting vigorous movements. Maleic acid and fumaric acid exhibit considerable difference in their capacity to lower the surface tension of water and this easily explains their difference in behaviour on the surface of water. The lowering produced by benzoic acid is 11.6 per cent., but its movements are more vigorous than those of maleic acid though the latter lowers to the extent of 12.22 per cent. This is due to the fact that maleic acid is more soluble in bulk and as a particle of it moves some distance it gets dissolved and thus disappears. *o*-Nitrophenol and phthalimide exhibit far more differences in their movements than is indicated by the surface tension of their solutions. It is thus evident that while the lowering of the surface tension of water is a necessary condition for exhibiting the movements on its surface the vigour and persistence of the movements are controlled by several other factors. The chief among them may be density, solubility, rate of solution on the surface or in bulk, rate of evaporation, etc.

During the course of the above investigations we had occasion to observe combination movements exhibited by two pairs of substances. When small pieces of phenyl-acetic* acid are added one after another to a clean water surface a stage is reached when they all remain steady without showing any movement. When on this surface a small piece of camphor is placed so that it does not touch any particle of phenyl acetic acid it is found that the camphor particle also remains steady. If however the camphor particle is

* Saturation of the water surface first with Camphor and subsequent addition of Phenyl acetic acid gives rise to more spectacular Combination movements.

made to come into contact with a particle of phenyl acetic acid these two form a couple and begin to move about very vigorously till their combination ceases by colliding either with the walls of the vessel or with any other bigger floating particle, and then both come to a stop. A similar combination is observed with the substances *p*-nitrotoluene and *o*-nitrophenol. In both these cases droplets of liquid are found to be shot out in the direction opposite to that of the movement. We are inclined to feel that these combination movements may be caused by the recoil effects produced when droplets of the molten substance leave the solid. The melting is obviously caused by each substance lowering the melting point of the other.

Summary

A large number of organic compounds belonging to different groups have been studied in regard to their behaviour on the surface of water. The influences of the various groups — COOH, > C = O, — NH₂, etc. in a substance on its behaviour on the water surface are discussed.

Percentage lowering of surface tension of aqueous solutions of a number of typical compounds are recorded and the results compared with their behaviour on the water surface.

Combination movements exhibited by the pairs phenylacetic acid—camphor and *p*-nitrotoluene—*o*-nitrophenol are described.

REFERENCES.

- | | |
|-----------------|----------------------------------------------------|
| 1. Geppert | .. <i>Physik. Zeit</i> , 1919, 20 , 78. |
| 2. Edwards | .. <i>J.C.S.</i> , 1925, 127 , 744 to 747. |
| 3. L. A. Ramdas | .. <i>Ind. Jour. Physics</i> , 1926, 1 , 1. |